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Dynamic Density Functional Simulation of Micelle and Vesicle Formation Process in Amphiphilic Block Copolymer Solutions

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我々は動的密度汎関数法によって両親媒性ブロックコポリマー溶液のミセル・ベシクル構造の形成ダイナミクスのシミュレーションを行った。シミュレーションの結果、一様な初期状態からミセルやベシクルが自発的に形成されることが確認された。得られたベシクル形成ダイナミクスはこれまでに報告されている粒子法シミュレーションの結果と定性的によく一致した。

1 Introduction

Amphiphilic block copolymers in selective solvent form various micellar structures (spherical micelles, cylindrical micelles and vesicles). The micellar structure formation dynamics have been studied by using the particle methods such as Brownian dynamics (BD) [1] or the dissipative particle dynamics (DPD) [2].

The continuum models, which is widely used for simulations of microphase separation structures of block copolymers, are expected to be useful for micellar systems, but most of works (the self consistent field (SCF) simulations [3] or the density functional (DF) simulations [4]) are limited to static (equilibrium) simulations. Quite recently, He and Schmid [5] studied the vesicle formation dynamics by the external potential dynamics (EPD), but unfortunately their result are qualitatively different from the results of particle method simulations. In this work, we show that the micelle and vesicle formation process similar to particle simulations can be reproduced by the DF simulation.

2 Theory

We use the following free energy functional [4] for AB diblock copolymer melts and S solvent mixtures. For simplicity we set $k_BT = 1$.

$$\begin{aligned} F = & \sum_{i\,(=A,B)} \int d\boldsymbol{r}\, 2f_i C_{ii} \psi_i^2(\boldsymbol{r}) \ln \psi_i(\boldsymbol{r}) + \int d\boldsymbol{r}\, 2\psi_S^2(\boldsymbol{r}) \ln \psi_S(\boldsymbol{r}) \\ & + \sum_{i,j\,(=A,B)} \int d\boldsymbol{r} d\boldsymbol{r}'\, 2\sqrt{f_i f_j} A_{ij} \tilde{\mathcal{G}}(\boldsymbol{r}-\boldsymbol{r}') \psi_i(\boldsymbol{r}) \psi_j(\boldsymbol{r}') + \sum_{i\,(=A,B,S)} \int d\boldsymbol{r}\, \frac{b^2}{6} |\nabla \psi_i(\boldsymbol{r})|^2 \\ & + \int d\boldsymbol{r}\, 4\sqrt{f_A f_B} C_{AB} \psi_A(\boldsymbol{r}) \psi_B(\boldsymbol{r}) + \sum_{i,j\,(=A,B,S)} \int d\boldsymbol{r}\, \frac{\chi_{ij}}{2} \psi_i^2(\boldsymbol{r}) \psi_j^2(\boldsymbol{r}) \end{aligned} \tag{1}$$

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where $\psi_i(\boldsymbol{r}) = \sqrt{\phi_i(\boldsymbol{r})}$ is the density ($i = A, B, S$), b is the Kuhn length, f_i is the block ratio of the i-subchain, A_{ij} and C_{ij} is calculated from b, f_i, and the polymerization index N. χ_{ij} is the Flory-Huggins χ parameter. $\tilde{\mathcal{G}}(\boldsymbol{r} - \boldsymbol{r}')$ is the Green function which satisfies $[-\nabla^2 + \lambda^2]\tilde{\mathcal{G}}(\boldsymbol{r} - \boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}')$.

We use the stochastic dynamic density functional equation [6] for the time evolution.

$$\frac{\partial \phi_i(\boldsymbol{r})}{\partial t} = \nabla \cdot \left[\frac{1}{\zeta_i} \phi_i(\boldsymbol{r}) \nabla \frac{\delta F}{\delta \phi_i(\boldsymbol{r})} \right] + \xi_i(\boldsymbol{r}) \tag{2}$$

where ζ_i is the friction coefficient of a segment in the i-subchain. $\xi_i(\boldsymbol{r}, t)$ is the thermal noise term which satisfies the following fluctuation dissipation relation.

$$\langle \xi_i(\boldsymbol{r}, t) \rangle = 0, \qquad \langle \xi_i(\boldsymbol{r}, t) \xi_j(\boldsymbol{r}', t') \rangle = -\frac{2}{\zeta_i} \tilde{\beta}^{-1} \delta_{ij} \nabla \cdot \left[\phi_i(\boldsymbol{r}) \nabla \delta(\boldsymbol{r} - \boldsymbol{r}') \right] \delta(t - t') \tag{3}$$

$\tilde{\beta}^{-1}$ is the magnitude of the noise and is not equal to $k_B T$. The value of $\tilde{\beta}^{-1}$ is determined from coarse-grained timescale [6]. Setting $\zeta_i = 1/2$ and rewriting eq (2) by using $\psi_i(\boldsymbol{r})$, we get the following dynamic equation.

$$\frac{\partial \phi_i(\boldsymbol{r})}{\partial t} = \psi_i(\boldsymbol{r}) \nabla^2 \mu_i(\boldsymbol{r}) - \mu_i(\boldsymbol{r}) \nabla^2 \psi_i(\boldsymbol{r}) + \xi_i(\boldsymbol{r}) \tag{4}$$

3 Simulation

Three dimensional simulations were carried out by solving eq (4) numerically. Parameters are set as follows; degree of polymerization $N = 10$, $f_A = 1/3, f_B = 2/3, \lambda = 5$, volume fraction of polymer $\bar{\phi}_p = 0.2$, $\chi_{AB} = 2.5, \chi_{AS} = -0.5, \chi_{BS} = 5, \tilde{\beta}^{-1} = 0.3125$. We observed the following vesicle formation process: At the first stage, small spherical micelles are formed rapidly. Then the spherical micelles aggregate and grow by collision, and form cylindrical or disk like micelles. Finally the disk like micelles close up spontaneously and form vesicles. This vesicle formation process qualitatively agrees well with the result of the particle simulations [1, 2]. We also observed that other micellar structures such as spherical micelles or bilayer structures are formed by chaining parameters (the χ parameter or the volume fraction of polymer $\bar{\phi}_p$).

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